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**Addition Reactions of a Silylated Imino(methylene)phosphorane**

by

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# Addition Reactions of a Silylated Imino(methylene)phosphorane

Donn A. DuBois and Robert H. Neilson\*

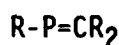
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## Abstract

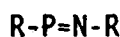
Reactions of the imino(methylene)phosphorane,  $(\text{Me}_3\text{Si})_2\text{NP}(=\text{NSiMe}_3)=\text{CHSiMe}_3$  (**2**), a stable 3-coordinate  $\text{P}^{\text{V}}$  species, with some electrophilic and nucleophilic reagents have been studied. Treatment of **2** with various chlorophosphines gave the novel  $\text{P}^{\text{V}}\text{-C-P}^{\text{III}}$  systems  $(\text{Me}_3\text{Si})_2\text{NP}(\text{Cl})(=\text{NSiMe}_3)\text{CH}(\text{SiMe}_3)\text{P}(\text{X})\text{R}$  [**3**:  $\text{R} = \text{X} = \text{Ph}$ ; **4**:  $\text{R} = \text{X} = \text{NMe}_2$ ; **5**:  $\text{R} = \text{Ph}$ ,  $\text{X} = \text{Cl}$ ] via addition across the  $\text{P}=\text{C}$  double bond. The  $\text{P-Cl}$  derivative **5** readily eliminated  $\text{Me}_3\text{SiCl}$  to afford the cyclic product **6**, an unusual  $\text{P}^{\text{V}}\text{NP}^{\text{III}}\text{C}$  four-membered ring system. Compound **2** also underwent rapid addition reactions with both secondary amines and  $\text{CF}_3\text{CH}_2\text{OH}$  to yield the four-coordinate aminophosphoranimines  $(\text{Me}_3\text{Si})_2\text{NP}(=\text{NSiMe}_3)(\text{CH}_2\text{SiMe}_3)\text{NR}_2$  (**7**:  $\text{R} = \text{Me}$ ; **8**:  $\text{R} = \text{Et}$ ) and the  $\text{P}$ -trifluoroethoxyphosphoranimine  $(\text{Me}_3\text{Si})_2\text{NP}(=\text{NSiMe}_3)(\text{CH}_2\text{SiMe}_3)\text{OCH}_2\text{CF}_3$  (**9**), respectively. Heating of **9** resulted in elimination of  $\text{Me}_3\text{SiOCH}_2\text{CF}_3$  and formation of the  $\text{P}_2\text{N}_2$  dimer,  $[\text{Me}_3\text{SiNP}(=\text{NSiMe}_3)\text{CH}_2\text{SiMe}_3]_2$  (**10**). Addition of methyllithium to **2**, followed by quenching of the intermediate carbanion with either  $\text{Me}_3\text{SiCl}$  or  $\text{Me}_2\text{SiCl}_2$ , gave the highly silylated  $\text{P}$ -methylphosphoranimines,  $(\text{Me}_3\text{Si})_2\text{NP}(\text{Me})(=\text{NSiMe}_3)\text{CH}(\text{SiMe}_3)\text{SiMe}_2\text{X}$  (**11**:  $\text{X} = \text{Me}$ ; **12**:  $\text{X} = \text{Cl}$ ). When heated, the chlorosilyl derivative **12** readily underwent loss of  $\text{Me}_3\text{SiCl}$  and cyclization to give a novel  $\text{PNCSi}$  four-membered ring product **13**. Based upon these representative reactions, the reactivity of the  $\text{P}=\text{C}$  bond in the imino(methylene)phosphorane **2** is contrasted with that in the analogous 2-coordinate  $\text{P}^{\text{III}}$  system, the (methylene)phosphine,  $(\text{Me}_3\text{Si})_2\text{NP}=\text{CHSiMe}_3$  (**1**).

## Introduction

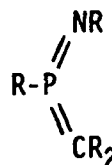
Since the first reports in the 1970's of the synthesis of stable (methylene)phosphines (A)<sub>III</sub> and imino-phosphines (B)<sub>III</sub>, the preparative chemistry,<sup>8</sup> reactivity,<sup>9</sup> and coordination chemistry<sup>10</sup> of these two-coordinate P<sup>III</sup> species have been developed to a considerable extent. In contrast, the imino(methylene)phosphoranes (C)<sub>V</sub> which contain both P=C and P=N functionalities in a trigonal planar P<sup>V</sup> arrangement, have received comparatively little attention. Studies of the derivative chemistry of such species should provide synthetically useful information regarding the relative reactivity of (1) a P=C double bond vs. a P=N double bond, and (2) similarly substituted P=C double bonds in P<sup>III</sup>(A) and P<sup>V</sup>(C) systems.



A

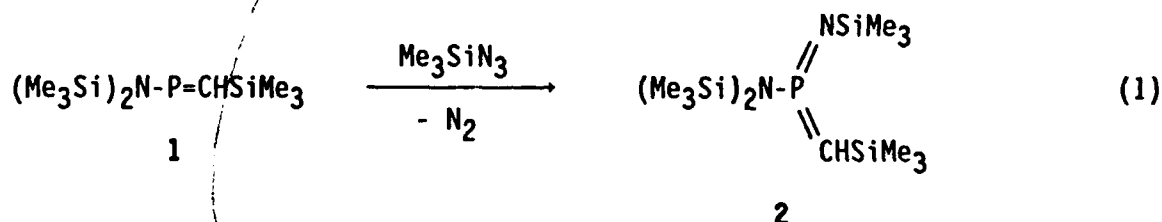


B



C

Recent work in our laboratory has involved the chemistry of the silylated (methylene)phosphine 1 which has been shown to undergo a variety of interesting addition, substitution, coordination and coupling reactions of the P=C moiety.<sup>7-10</sup> The oxidation of 1 with trimethylsilyl azide (eq 1) occurs smoothly to yield the imino(methylene)phosphorane 2 in high yield as a stable, distillable liquid.<sup>10</sup> As a continuation of these studies of the chemistry of P=C bonds, we report here the reactions of the three-coordinate P<sup>V</sup> derivative 2 with selected electrophilic and nucleophilic reagents.

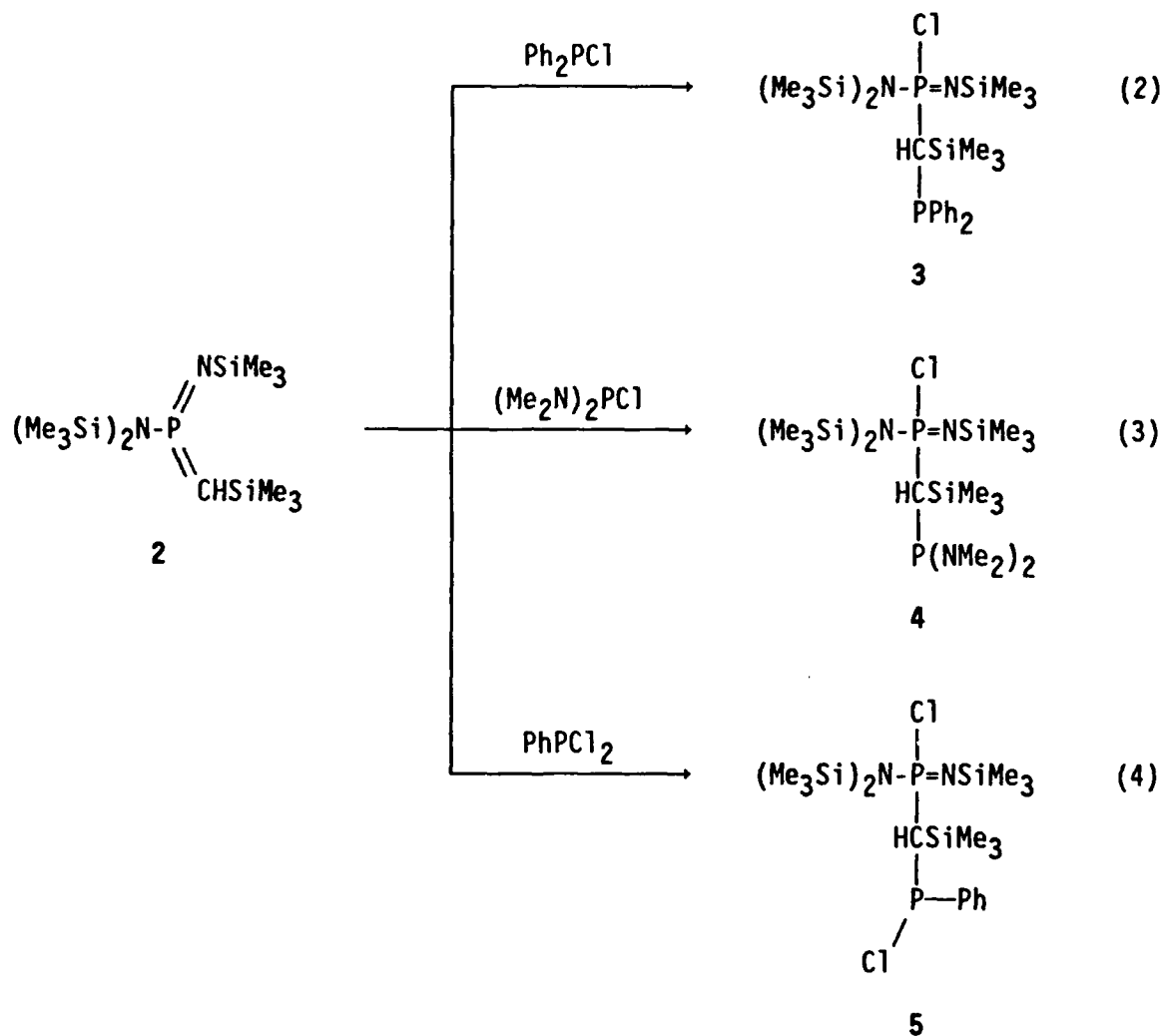


phosphines, silanes, methylene.

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## Results and Discussion

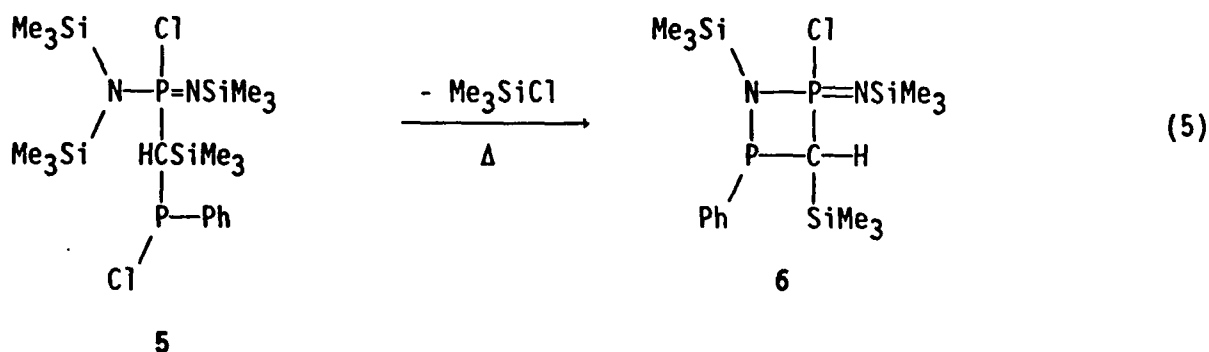
In order to compare the reactivity of the imino(methylene)phosphorane **2** with the known chemistry of the (methylene)phosphine **1**, the reactions of **2** with three types of reagents (chlorophosphines, secondary amines, and methyllithium) were studied. A variety of different chlorophosphines reacted smoothly with **2** (eqs 2-4) at 0°C in dichloromethane solution to yield the P<sup>V</sup>-C-P<sup>III</sup> derivatives **3** - **5** as a result of addition across the P=C bond in **2**.



After solvent removal, compound **3** was obtained as a viscous yellow oil which gave a satisfactory elemental analysis but underwent extensive decomposition upon attempted distillation. The NMR spectral data (Table 1) for the undistilled material is in complete agreement with the proposed structure. In addition to

the expected  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals observed for the  $\text{Me}_3\text{Si}$  and phenyl groups, the central proton of the  $\text{CH}(\text{SiMe}_3)$  group gives rise to two sets of doubled-doublet patterns, consistent with the presence of two chiral centers ( $\text{CH}$  and  $\text{P}^{\text{V}}$ ) and, hence, diastereomers. The existence of diastereomers for 4 and 5 is also shown by some of the NMR signals (i.e., the  $\text{NMe}_2$  proton and carbon resonances of 4 and the  $^{31}\text{P}$  peaks of 5). Compound 4 is considerably more volatile than the  $\text{PPh}_2$  analogue 3 and could be purified by distillation under reduced pressure without decomposition.

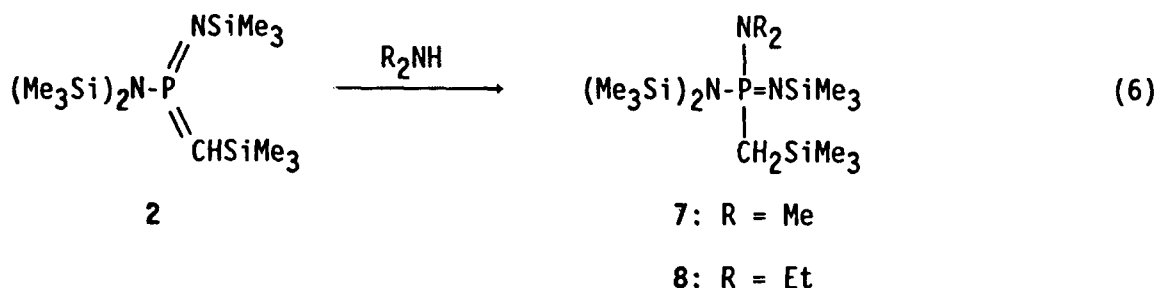
The NMR spectra obtained on the chlorophosphine derivative 5 prior to distillation indicated the presence of a second product 6 (ca. 4:1 ratio of 5 to 6). When the mixture was heated at ca.  $100^\circ\text{C}$ , 5 was completely converted to the cyclic derivative 6 (eq 5) by elimination of  $\text{Me}_3\text{SiCl}$ . Compound 6, an example of a rare type of  $\text{P}_2\text{NC}$  ring system containing both  $\text{P}^{\text{III}}$  and  $\text{P}^{\text{V}}$  centers,<sup>11</sup> was isolated by distillation in 72% yield as a clear viscous liquid and was fully characterized by NMR spectroscopy (Table 1), elemental analysis, and mass spectroscopy. Confirming evidence of the presence of a  $\text{P}^{\text{III}}$  center in 6 was obtained by its facile reaction with  $\text{Fe}_2(\text{CO})_9$  which apparently gave the expected  $\text{Fe}(\text{CO})_4$  complex. Although this complex was thermally unstable, and thus not well characterized, its  $^{31}\text{P}$  NMR spectrum showed the expected<sup>12</sup> downfield shift of the  $\text{P}^{\text{III}}$  signals (see Experimental) and the same relative proportion of diastereomers as observed for 6.



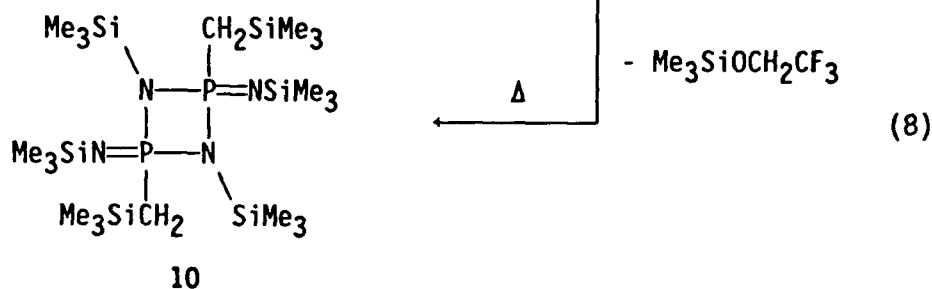
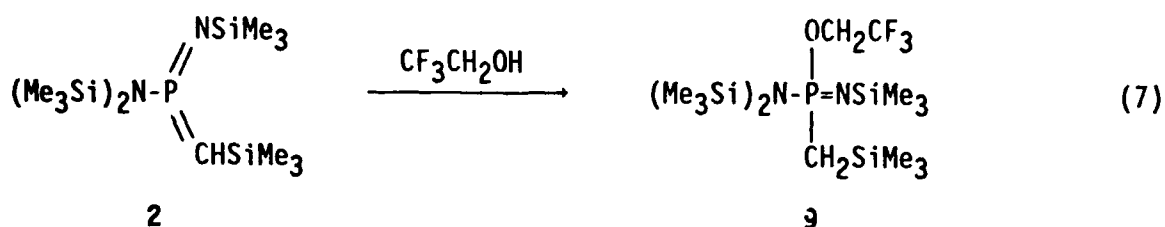
Toward these chlorophosphine reagents, the  $\text{P}=\text{C}$  double bond in the imino(methylene)phosphorane 2 is much more reactive than that in the (methylene)phosphine 1. In fact, 1 only slowly adds  $\text{Ph}_2\text{PCl}$  to afford a  $\text{P}-\text{C}-\text{P}$  derivative<sup>8</sup> and does not react at all with either  $(\text{Me}_2\text{N})_2\text{PCl}$  or  $\text{PhPCl}_2$ . Since  $\text{PhPCl}_2$  is more electrophilic than  $\text{Ph}_2\text{PCl}$ , this suggests that nucleophilic attack of the chlorophosphine on the highly

electrophilic 2-coordinate  $P^{III}$  center (1) is the important mechanistic feature in the case of 1. On the other hand, in the  $P^V$  analogue 2, the nucleophilic character of the carbon end of the more polar  $P^{\delta+}=C^{\delta-}$  bond is probably responsible for its higher reactivity toward electrophilic species such as  $PhPCl_2$ .

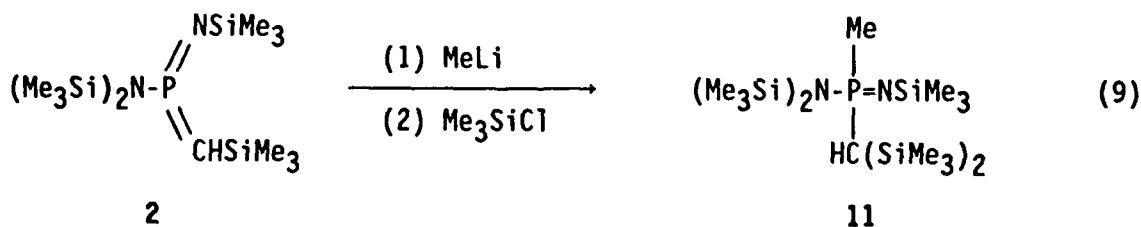
An even more striking contrast in the chemistry of these 2- and 3-coordinate  $P=C$  species is found in their reactions with certain protic reagents, especially secondary amines. We have previously reported that 1 reacts with diethylamine in a complex manner that involves not only addition to the  $P=C$  bond but also Si-N bond cleavage and other processes, leading eventually to novel P-N-H or N=P-P systems depending on the exact reaction conditions.<sup>7</sup> The reactions of the imino(methylene)phosphorane 2 with secondary amines (eq 6), however, are much more straightforward and involve simple addition to the  $P=C$  bond. The new aminophosphoranes 7 and 8 were isolated as colorless liquids and characterized by NMR spectroscopy (Table 1) prior to distillation. Both compounds underwent thermal decomposition to unidentified product mixtures upon attempted distillation.



We have also previously reported that methanol reacts with 2 (as it does with 1) via simple addition to the  $P=C$  bond.<sup>10</sup> As part of the present study, compound 2 was treated with one equivalent of  $\text{CF}_3\text{CH}_2\text{OH}$  to yield the P-trifluoroethoxyphosphoranimine 9 (eq 7) as a stable, distillable liquid. When a neat sample of 9 was heated in a sealed glass tube at  $190^\circ\text{C}$ , the  $P_2N_2$  ring system 10 (mixture of *cis* and *trans* isomers)<sup>13</sup> was produced in quantitative yield as a result of elimination of  $\text{Me}_3\text{SiOCH}_2\text{CF}_3$  (eq 8). The elimination of this silane is also utilized in the synthesis of poly(alkyl/arylphosphazenes),  $[\text{R}_2\text{PN}]_n$ , from simpler phosphoranimines,  $\text{Me}_3\text{SiN}=\text{P}(\text{OCH}_2\text{CF}_3)\text{R}_2$ .<sup>14</sup>



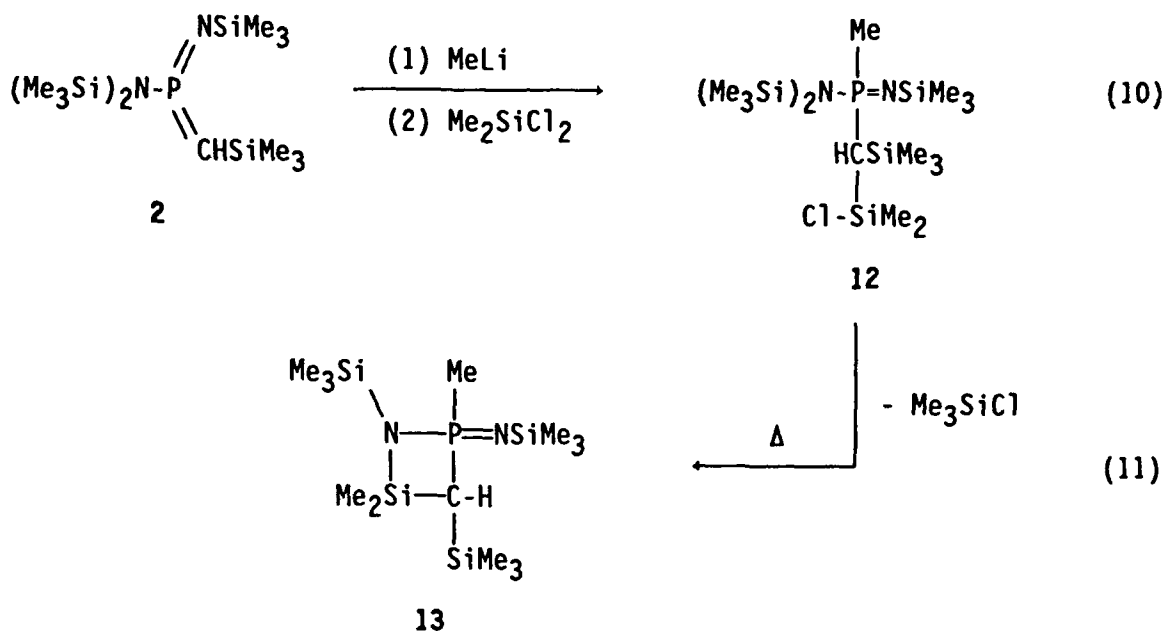
The reaction of the imino(methylene)phosphorane **2** with a strong nucleophilic reagent, methyllithium, also occurred exclusively via addition to the P=C bond (eq 9). After quenching the intermediate carbanion with  $\text{Me}_3\text{SiCl}$ , this reaction afforded the pentakis(trimethylsilyl)-substituted phosphoranimine **11** as a fully characterized, distillable liquid. Similar reactions of the (methylene)phosphine **1** with alkyl lithium compounds are also much more complicated. For example, when treated with  $\text{MeLi}$ , **1** undergoes nucleophilic displacement of the  $(\text{Me}_3\text{Si})_2\text{N}$  group from phosphorus and further additions to the P=C moiety to yield a novel P-C-P derivative.<sup>9</sup>



Interestingly, during the distillation of compound **11** at ca.  $110^\circ\text{C}$  under reduced pressure, partial rearrangement to a more symmetrical structural isomer,  $(\text{Me}_3\text{Si})_2\text{NP}(=\text{NSiMe}_3)(\text{CH}_2\text{SiMe}_3)_2$  (**11a**) was observed. The presence of this isomer (as ca. 10-20% of the distillate) was confirmed by the appearance of a second  $^{31}\text{P}$  NMR signal ( $\delta$  5.9) that was split into a clear quintet ( $^2J_{\text{PH}} = 20.8$  Hz) upon proton-coupling. The isomeric mixture of **11** and **11a**, although not separable by fractional distillation, gave a satisfactory elemental analysis.



The carbanion generated in the reaction of the imino(methylene)phosphorane **2** with MeLi was also treated with one equivalent of dimethyldichlorosilane (eq 10) to give an unstable chlorosilyl derivative **12**. Attempted distillation of **12** resulted in facile elimination of Me<sub>3</sub>SiCl (eq 11) and closure to the novel PNCSi four-membered ring system **13**. Compound **13** was identified by NMR spectroscopy (Table 1) and elemental analysis.



In summary, the important results of this study are (1) that the imino(methylene)phosphorane **2** readily undergoes addition of both electrophilic and nucleophilic reagents *selectively to the P=C double bond*, (2) that these reactions are generally more straightforward than they are with the 2-coordinate P<sup>III</sup> analogue **1**, and (3) that the reactions involving difunctional reagents (e.g., PhPCl<sub>2</sub> or Me<sub>2</sub>SiCl<sub>2</sub>) can be useful for the preparation of some unusual small ring phosphorus compounds.

## Experimental Section

**Materials and General Procedures.** The following reagents were obtained from commercial sources and used without further purification:  $\text{PCl}_3$ ,  $\text{PhPCl}_2$ ,  $\text{Ph}_2\text{PCl}$ ,  $\text{Me}_2\text{NH}$ ,  $\text{Et}_2\text{NH}$ ,  $\text{MeLi}$ ,  $\text{Fe}_2(\text{CO})_9$ ,  $\text{Me}_3\text{SiCl}$ ,  $\text{Me}_2\text{SiCl}_2$ ,  $\text{Me}_3\text{SiNMe}_2$ , and  $\text{CF}_3\text{CH}_2\text{OH}$ . Bis(dimethylamino)(chloro)phosphine,  $(\text{Me}_2\text{N})_2\text{PCl}$ ,<sup>15</sup> was prepared by the addition of two molar equivalents of  $\text{Me}_3\text{SiNMe}_2$  to  $\text{PCl}_3$  in ether at  $0^\circ\text{C}$ . The imino(methylene)phosphorane **2** was prepared according to the published procedure.<sup>10</sup> Ether, pentane, and  $\text{CH}_2\text{Cl}_2$  were distilled from  $\text{CaH}_2$  and THF was distilled from sodium/benzophenone immediately prior to use. Proton and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Varian XL-300 spectrometer;  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were obtained on a JEOL FX-60 instrument. Mass spectra were obtained on a Finnigan GC-MS instrument. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The following procedures are representative of those used for the synthesis of the new compounds prepared in this study.

**Preparation of  $(\text{Me}_3\text{Si})_2\text{NP}(\text{Cl})(=\text{NSiMe}_3)\text{CH}(\text{SiMe}_3)\text{PPh}_2$  (**3**).** A 100-mL flask, equipped with a magnetic stirrer,  $\text{N}_2$  inlet, and a septum, was charged with the imino(methylene)phosphorane **2** (10.0 mmol) and  $\text{CH}_2\text{Cl}_2$  (30 mL). The solution was cooled to  $0^\circ\text{C}$  and  $\text{Ph}_2\text{PCl}$  (10.0 mmol) was added slowly via syringe to the stirred mixture. After ca. 30 minutes, the mixture was allowed to warm to room temperature and was stirred for ca. one hour. Solvent removal left **3** as a viscous, light yellow liquid that was identified by NMR spectroscopy (Table 1). *Anal.* Calcd: C, 51.29; H, 8.09. Found: C, 51.11; H, 8.03. Attempts to distill **3** under reduced pressure (0.01 mm) led to extensive decomposition.

**Preparation of  $(\text{Me}_3\text{Si})_2\text{NP}(\text{Cl})(=\text{NSiMe}_3)\text{CH}(\text{SiMe}_3)\text{P}(\text{NMe}_2)_2$  (**4**).** In a similar fashion, compound **2** (20.0 mmol) was treated with an equimolar amount of  $(\text{Me}_2\text{N})_2\text{PCl}$  to afford **4** as a distillable, colorless liquid (74% yield, bp  $96^\circ\text{C}/0.01$  mm). *Anal.* Calcd: C, 39.31; H, 9.95. Found: C, 39.81; H, 9.60.

**Preparation of  $(\text{Me}_3\text{Si})_2\text{NP}(\text{Cl})(=\text{NSiMe}_3)\text{CH}(\text{SiMe}_3)\text{P}(\text{Cl})\text{Ph}$  (**5**) and the Cyclic Derivative **6**.** Using the same procedure,  $\text{PhPCl}_2$  (10.0 mmol) was added to a stirred solution of **2** (10.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL). After the mixture was allowed to warm to room temperature, the solvent was removed under reduced

pressure. Analysis of the crude yellow liquid by NMR spectroscopy (Table 1) showed that a mixture of **5** and **6** was present. This mixture was then heated at 100°C for ca. one hour and Me<sub>3</sub>SiCl was removed under reduced pressure and identified by its <sup>1</sup>H NMR spectrum. From the orange residue, **6** was isolated by fractional distillation as a colorless liquid (72% yield, bp 106-110°C/0.01 mm). *Anal.* Calcd: C, 44.16; H, 7.71. Found: C, 44.01; H, 7.86. The mass spectrum of **6** showed a molecular ion (M<sup>+</sup>) at 434 *m/e* and a base peak at 419 *m/e* (M<sup>+</sup> - CH<sub>3</sub>).

**Reaction of 2 with Fe(CO)<sub>4</sub>.** Compound **2** (2.0 mmol) was added via syringe to a stirred suspension of Fe<sub>2</sub>(CO)<sub>9</sub> (2.0 mmol) in pentane (25 mL) and the mixture was stirred overnight at room temperature. Solvent removal gave a very viscous red oil that was characterized by <sup>31</sup>P NMR spectroscopy [diastereomers: δ -22.8, 111.7 (J<sub>PP</sub> = 41.5 Hz); δ -12.8, 101.8 (J<sub>PP</sub> = 34.2 Hz)]. This Fe(CO)<sub>4</sub> complex of **2** was too thermally unstable for elemental analysis and it resisted all attempts at recrystallization.

**Preparation of (Me<sub>3</sub>Si)<sub>2</sub>NP(=NSiMe<sub>3</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)NR<sub>2</sub> (**7**: R = Me; **8**: R = Et).** In a typical experiment, Et<sub>2</sub>NH (20.0 mmol) was added via syringe to a stirred solution of **2** (20.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> at 0°C. The mixture was allowed to warm to room temperature and was stirred for one hour. Solvent removal gave **8** as a pale yellow liquid which was easily characterized by NMR spectroscopy (Table 1). Attempts to distill the product under reduced pressure (0.01 mm), however, resulted in decomposition to unidentified products (with several <sup>31</sup>P NMR signals in the range of δ -10 to -25). The Me<sub>2</sub>N analogue **7** was prepared by a similar procedure except that the amine, measured as a liquid at -78°C, was allowed to bubble slowly into the solution of **2**. The product **7** was similarly unstable to distillation but a satisfactory elemental analysis was obtained on a sample prior to distillation. *Anal.* Calcd: C, 43.96; H, 10.82. Found: C, 43.67; H, 10.81.

**Preparation of (Me<sub>3</sub>Si)<sub>2</sub>NP(=NSiMe<sub>3</sub>)(OCH<sub>2</sub>CF<sub>3</sub>)CH<sub>2</sub>SiMe<sub>3</sub> (**9**).** A 250-mL flask, equipped with a magnetic stirring bar, N<sub>2</sub> inlet, and a septum was charged with Et<sub>2</sub>O (40 mL) and **2** (20.0 mmol). This solution was cooled to 0° an equimolar amount of CF<sub>3</sub>CH<sub>2</sub>OH was added slowly via syringe. The reaction mixture was allowed to warm to room temperature. Solvent removal left a white wax-like solid. Distillation gave **9** as a colorless liquid (80% yield, bp 86°C/0.1 mm) which crystallized on standing at room temperature. *Anal.* Calcd: C, 38.76; H, 8.67. Found: C, 38.48; H, 8.44.

**Preparation of  $[\text{Me}_3\text{SiNP}(=\text{NSiMe}_3)\text{CH}_2\text{SiMe}_3]_2$  (10).** A neat sample of freshly distilled **10** (10.0 mmol) was sealed under vacuum in a heavy-walled glass ampule. The ampule was heated at 190° for three days in a thermoregulated oven during which time the color of the sample changed from colorless to light brown. The  $\text{Me}_3\text{SiOCH}_2\text{CF}_3$  byproduct (98% yield) was removed under vacuum and identified by  $^1\text{H}$  NMR spectroscopy. The solid residue, which could be recrystallized from cold hexane, was subsequently identified as the dimer **10**. *Anal.* Calcd: C, 41.05; H, 9.99. Found: C, 40.78; H, 9.94.

**Preparation of  $(\text{Me}_3\text{Si})_2\text{NP}(\text{Me})(=\text{NSiMe}_3)\text{CH}(\text{SiMe}_3)_2$  (11).** A 250-mL flask, equipped with a magnetic stirring bar,  $\text{N}_2$  inlet, and a septum, was charged with the imino(methylene)phosphorane **2** (16.0 mmol) and THF (30 mL). The mixture was cooled to -78°C and MeLi (16.0 mmol, 1.4 M in  $\text{Et}_2\text{O}$ ) was added via syringe. After the mixture was stirred for one hour at -78°C, an equimolar amount of  $\text{Me}_3\text{SiCl}$  was added and the mixture was allowed to warm slowly to room temperature. Hexane (ca. 30 mL) was added and the white solid ( $\text{LiCl}$ ) was allowed to settle. The supernatant solution was decanted from the solid and the solvents were removed under reduced pressure. Distillation afforded **11** as a colorless liquid (61% yield, bp 108-110°C). *Anal.* Calcd: C, 45.08; H, 10.90. Found: C, 44.99; H, 10.55. A small amount (ca. 10%) of the structural isomer **11a** was observed by  $^{31}\text{P}$  NMR spectroscopy in the distilled product (see text).

**Preparation of  $(\text{Me}_3\text{Si})_2\text{NP}(=\text{NSiMe}_3)(\text{Me})(\text{CHSiMe}_3)\text{SiMe}_2\text{Cl}$  (12) and the Cyclic Derivative 13.** A 250-mL flask, equipped with a magnetic stirring bar,  $\text{N}_2$  inlet, and a septum was charged with THF (40 mL) and **2** (16.0 mmol). After cooling this mixture to -78°C, MeLi (16.0 mmol, 1.4 M in  $\text{Et}_2\text{O}$ ) was added slowly via syringe. The solution of the resulting anion was allowed to stir at -78°C for 30 min. Dimethyldichlorosilane (16.0 mmol) was added via syringe and the reaction mixture was allowed to warm to room temperature. Isolation of the product as described above for **11** left a colorless residue that, by NMR spectroscopic analysis (Table 1), was identified as compound **12**. Attempts to distill **12** led to elimination of  $\text{Me}_3\text{SiCl}$  to afford the cyclic derivative **13** as a colorless liquid (61% yield, bp 108-110°/0.04 mm). *Anal.* Calcd: C, 45.06; H, 10.92. Found: C, 44.87; H, 10.55.

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**Table I.** Selected NMR Spectroscopic Data<sup>a</sup>

Compound	Signal	<sup>1</sup> H NMR		<sup>13</sup> C NMR		<sup>31</sup> P NMR
		δ	J <sub>PH</sub> <sup>b</sup>	δ	J <sub>PC</sub> <sup>b</sup>	δ <sup>c</sup>
$  \begin{array}{c}  \text{Cl} \\    \\  (\text{Me}_3\text{Si})_2\text{N}-\text{P}=\text{NSiMe}_3 \\    \\  \text{Ph}_2\text{P}-\text{C}(\text{H})-\text{SiMe}_3 \\  \mathbf{3}  \end{array}  $	PCH <sup>d</sup>	2.84	26.4	40.28	39.7	-10.0
			2.9		-0.0	18.6
		3.07	20.5			(151.4)
			4.4			
$  \begin{array}{c}  \text{Cl} \\    \\  (\text{Me}_3\text{Si})_2\text{N}-\text{P}=\text{NSiMe}_3 \\    \\  (\text{Me}_2\text{N})_2\text{P}-\text{C}(\text{H})-\text{SiMe}_3 \\  \mathbf{4}  \end{array}  $	PCH	2.18	17.2	39.44	51.7	3.2
			2.5		29.6	70.3
	NCH <sub>3</sub> <sup>d,e</sup>	2.55	12.2	39.23	16.7	(24.4)
		2.61	20.0	35.93	4.0	
$  \begin{array}{c}  \text{Cl} \\    \\  (\text{Me}_3\text{Si})_2\text{N}-\text{P}=\text{NSiMe}_3 \\    \\  \text{Ph}-\text{P}(\text{Cl})-\text{C}(\text{H})-\text{SiMe}_3 \\  \mathbf{5}  \end{array}  $	CH	2.88	21.5	52.93	42.3	0.2 <sup>f</sup>
			2.0		29.2	25.8
						(43.9)
						-1.9 <sup>f</sup>
						21.4
$  \begin{array}{c}  \text{Me}_3\text{Si} \quad \text{Cl} \\  \diagdown \quad   \\  \text{N} \quad \text{P}=\text{NSiMe}_3 \\    \quad   \\  \text{P} \quad \text{C}-\text{H} \\    \quad   \\  \text{Ph} \quad \text{SiMe}_3 \\  \mathbf{6}  \end{array}  $	CH <sup>d,e</sup>	2.78	23.9	53.30	64.5	-4.9 <sup>f</sup>
			4.4		29.2	13.2
		2.92	22.0	53.05	64.4	(43.9)
			3.9		29.2	-2.1 <sup>f</sup>
						12.8
						(24.0)



Table I. continued

Compound	Signal	<sup>1</sup> H NMR		<sup>13</sup> C NMR		<sup>31</sup> P NMR
		δ	J <sub>PH</sub>	δ	J <sub>PC</sub>	δ
$  \begin{array}{c}  \text{NMe}_2 \\    \\  (\text{Me}_3\text{Si})_2\text{N}-\text{P}=\text{NSiMe}_3 \\    \\  \text{CH}_2\text{SiMe}_3  \end{array}  $	NCH <sub>3</sub>	2.46	11.1	37.28	3.3	20.1
	PCH <sub>2</sub>	1.19	17.6	23.06	102.0	
7						
$  \begin{array}{c}  \text{NEt}_2 \\    \\  (\text{Me}_3\text{Si})_2\text{N}-\text{P}=\text{NSiMe}_3 \\    \\  \text{CH}_2\text{SiMe}_3  \end{array}  $	PCH <sub>2</sub>	1.25	18.2	23.16	105.1	19.1
	NCH <sub>2</sub>	2.94 <sup>g</sup>		40.72	5.1	
	CH <sub>3</sub>	1.10	(7.0) <sup>h</sup>	15.06	5.4	
8						
$  \begin{array}{c}  \text{OCH}_2\text{CF}_3 \\    \\  (\text{Me}_3\text{Si})_2\text{N}-\text{P}=\text{NSiMe}_3 \\    \\  \text{CH}_2\text{SiMe}_3  \end{array}  $	PCH <sub>2</sub>	1.36	20.5	24.68	109.1	18.9
	OCH <sub>2</sub>	3.9 - 4.3 <sup>g</sup>		59.48	3.5	
					(36.1) <sup>j</sup>	
	CF <sub>3</sub>			124.20	12.9	
9					(276.5) <sup>j</sup>	
$  \begin{array}{c}  \text{Me}_3\text{Si} \quad \text{CH}_2\text{SiMe}_3 \\  \diagdown \quad   \\  \text{N} \quad \text{P}=\text{NSiMe}_3 \\    \quad   \\  \text{Me}_3\text{SiN}=\text{P} \quad \text{N} \\    \quad   \\  \text{Me}_3\text{SiCH}_2 \quad \text{SiMe}_3  \end{array}  $	PCH <sub>2</sub>	1.66 <sup>d</sup>	20.6	29.42 <sup>e</sup>	11.2	-11.9 <sup>f</sup>
		1.51	19.6	26.84	14.0	-21.33
10						

Table I. continued

Compound	Signal	<sup>1</sup> H NMR		<sup>13</sup> C NMR		<sup>31</sup> P NMR
		δ	J <sub>PH</sub>	δ	J <sub>PC</sub>	δ
$  \begin{array}{c}  \text{Me} \\    \\  (\text{Me}_3\text{Si})_2\text{N}-\text{P}=\text{NSiMe}_3 \\    \\  \text{HC}(\text{SiMe}_3)_2  \end{array}  $	CH	1.30	21.1	27.89	77.8	18.0
	PMe	1.49	13.1	26.62	68.3	
11						
$  \begin{array}{c}  \text{Me} \\    \\  (\text{Me}_3\text{Si})_2\text{N}-\text{P}=\text{NSiMe}_3 \\    \\  \text{HCSiMe}_3 \\    \\  \text{Cl-SiMe}_2  \end{array}  $	PMe	1.46	12.4	25.97	75.1	9.7
	PCH	1.80	13.4	26.76	68.5	
12						
$  \begin{array}{c}  \text{Me}_3\text{Si} \quad \text{Me} \\  \diagdown \quad   \\  \text{N}-\text{P}=\text{NSiMe}_3 \\    \quad   \\  \text{Me}_2\text{Si}-\text{C}-\text{H} \\    \\  \text{SiMe}_3  \end{array}  $	PMe	1.49	12.2	27.62	77.0	18.0
	PCH	1.41	16.2	26.62	66.2	
13						

**Table I. continued**

<sup>a</sup>Chemical shifts relative to Me<sub>4</sub>Si for <sup>1</sup>H and <sup>13</sup>C spectra and to H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P spectra; coupling constants in Hz. Solvents: CDCl<sub>3</sub> or CH<sub>2</sub>Cl<sub>2</sub>. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of these compounds also exhibited the appropriate resonances for MeSi and Ph moieties as expected. <sup>b</sup>For a given signal, the larger J<sub>PH</sub> or J<sub>PC</sub> values are assigned to the P<sup>V</sup> center. <sup>c</sup>Upfield δ values assigned to P<sup>V</sup>; J<sub>PP</sub> values in parentheses. <sup>d</sup>Diastereomers observed in <sup>1</sup>H spectrum. <sup>e</sup>Diastereomers observed in <sup>13</sup>C spectrum. <sup>f</sup>Diastereomers observed in <sup>31</sup>P spectrum. <sup>g</sup>Complex multiplet. <sup>h</sup>J<sub>HH</sub> values in parentheses. <sup>i</sup>J<sub>FC</sub> values in parentheses.